

LEVEL II



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## HgCdTe SURFACE STUDY PROGRAM

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<p>The cleaved &lt;110&gt; surface of HgCdTe has been investigated using photoemission spectroscopy (PS) and Auger electron spectroscopy (AES). The results have been compared to CdTe. States due to Hg in the lattice were identified. The cleaved surface of p-type solid-state recrystallized (SSR) HgCdTe is seen to be enriched in Hg and shows no evidence of out-diffusion in a high vacuum (10<sup>-10</sup> torr). The surface shows no adsorption of dry molecular oxygen. Exposure to</p>		

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excited oxygen results in growth of Te-oxide. AES on epitaxial HgCdTe before and after ion bombardment indicates that bombardment significantly perturbs the composition of the surface region.

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## SUMMARY

The current phase of the program emphasizes the characterization of the atomically clean  $\langle 110 \rangle$  surface of HgCdTe. This surface is obtained by cleaving bulk-grown single-crystal sections in high vacuum ( $\sim 10^{-10}$  torr). The electronic structure, surface composition, and chemical properties are measured. These are obtained primarily from photoemission spectroscopy (PS) and Auger electron spectroscopy (AES). Some sputter Auger experiments have begun on epitaxial surfaces and anodic oxide layers principally to calibrate the apparatus for a later phase of the program.

Results have been obtained on  $\text{Hg}_{0.69}\text{Cd}_{0.31}\text{Te}$  before and after exposure to molecular oxygen and oxygen excited by the filament of an ion gauge. Comparison of the resulting energy distribution curves to that of CdTe indicates valence band states due to mercury (Hg) in the alloy. No Hg loss could be detected from the cleaved surface in a vacuum for periods up to several days. Also, no change could be detected in the spectra after exposure to atmospheric levels of molecular oxygen. This indicates a lack of  $\text{O}_2$  adsorption on the cleaved surface. Excited oxygen, however, shows core levels and valence band states due to chemically combined oxygen. The tellurium (Te) core level is shifted to higher energy by 3.5 eV, indicating the presence of a Te-oxygen bond.

The use of AES on HgCdTe before and after ion bombardment indicates that bombardment significantly perturbs the composition of the surface region.

Study of the cleaved surface will expand to include all the samples listed in Table 1 on page 5. Future work will concentrate on non-ideal surfaces and interface characterization.

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## Section 1 INTRODUCTION

This report covers the first half year of a two-year contract authorized by the Defense Advanced Research Projects Administration (DARPA). The purpose is to develop a microscopic model of the  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  surface which will contribute to the development of a proper surface passivation. The work is being performed under DARPA Contract MDA-903-80-C-0496 at Santa Barbara Research Center (SBRC) and Stanford University.

The first period of the surface study program will concentrate primarily on the characterization of the  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  surface; its electronic structure, composition, stability, and surface chemistry. The nature of surface and interface states, the stability or diffusion of mercury (Hg) in the crystal lattice, and the effects of a passivation layer are expected to play a crucial role in determining the electrical characteristics of devices such as infrared photovoltaic detectors or charge-coupled devices fabricated in mercury cadmium telluride ( $\text{HgCdTe}$ ). Ultraviolet photoemission spectroscopy (UPS), X-ray photoemission spectroscopy (XPS), and Auger electron spectroscopy (AES) provide information on the electronic states of a solid, the composition, and the surface and bulk chemistry,<sup>1</sup> and are used here to investigate the electronic structure of  $\text{HgCdTe}$ .

To obtain the clearest view possible of the underlying physical processes occurring at the surface, the atomically clean  $\langle 110 \rangle$  surface produced by cleaving bulk crystals in an ultra-high vacuum is used. UPS is used to probe the valence band and atomic core levels. Comparison of this information to the same measurements made on  $\text{CdTe}$  gives information on the manner in which Hg is bonded in the lattice. By comparing core level amplitudes from different escape depths, any change in element concentration with depth can be determined. The primary interest here is on Hg diffusion and possible loss from the surface.

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<sup>1</sup>W.E. Spicer, "Use of Photoemission and Related Techniques to Study Device Fabrication in Nondestructive Evaluation of Semiconductor Materials and Devices," ed. by J.N. Zemel, Plenum Publishing Corp. (1979).



Measurements of oxygen adsorption were made with UPS after the surface was exposed to dry unexcited oxygen and oxygen that had been excited by the filament of an ion gauge. The full valence band as well as the Hg and Cd core levels were probed using 21.2-eV radiation from a Hg discharge. Any shifts seen in these core levels after oxygen exposure are indication of bond changes and can be used to help determine the nature of the native oxide.

While AES, UPS and XPS as analytic tools can give information over depths of the order of 10 to 100Å from the surface, these will not be sufficient to probe material and interfaces which may be up to several thousand Å below the surface. To get accurate depth profiles, a known amount of material must be removed to expose a new surface to our measurement techniques. The appropriate method to do this is by ion sputtering of the surface. This permits surface characterization by AES during the material removal process and avoids possible contamination of the surface during removal of the sample from the vacuum as would be required for an etch. As an initial calibration of the etch rate, a series of anodic oxide films was prepared on HgCdTe wafers. These are in the range 500 to 1000Å thick. When the sputtering process has reached the oxide-wafer interface, a change in elemental abundance will be evident. At a constant ion flux, the film thickness divided by the time until the abundance change is seen gives an estimate of the sputter rate. As the sputter rate is highly matrix-dependent, the rate for the surface of the anodic oxide, the bulk of the oxide, the oxide-wafer interface, and the wafer bulk are all expected to be different; so that the rate given by measurement of these films is actually a weighted average of these rates and must be interpreted with care.

The effect of the sputter process itself on HgCdTe is also being investigated with simultaneous ion sputtering and AES of unoxidized surfaces. Quantification of the effects of this process is crucial to the determination of elemental abundance and its change at surfaces and interfaces, and will be addressed in detail during the next half year of this program.

## Section 2

### SAMPLE PREPARATION

This series of experiments concentrates primarily on the  $\langle 110 \rangle$  surface of material grown by solid-state recrystallization (SSR). However, some results are reported here of a preliminary look at the  $\langle 111 \rangle$  epitaxial surface. The bulk material is p-type due to Hg vacancies (a result of the high processing temperature) at about  $10^{16} \text{ cm}^{-3}$ . Material of this type is frequently annealed to a lower carrier concentration before being used in devices. Annealing is a process of diffusing Hg into the lattice by placing the material in a high-pressure Hg atmosphere at an elevated temperature so that Hg will be absorbed and diffuse into the bulk. The dimensions of the samples used in this phase of the program, however, are so large as to preclude effective annealing by Hg diffusion; therefore the as-grown material is used. These samples are prepared as blocks  $5 \times 5 \times 10 \text{ mm}$  with the long axis in the  $\langle 110 \rangle$  direction as shown in Figure 1. They are cleaved by application of pressure from opposing knife edges which expose the  $\langle 110 \rangle$  surface and give a cross section of  $0.25 \text{ cm}^2$  for experimentation. Hall characterization of one of these crystals has been completed and is shown in Figure 2. The remainder of the samples are in the process of being characterized, and are expected to be represented as a class by the data shown. Table 1 lists the material to be used for the studies of the cleaved surface.

The epitaxial surfaces provided for this study are liquid phase epitaxy (LPE) layers grown on HgCdTe and CdTe substrates. Table 2 lists the material provided to date and represents the very beginning of this portion of the program. This material is grown in a vertical "infinite melt" system utilizing either a Hg-rich solution with small additions of Cd and Te or a Te-rich solution with addition of Hg and Cd. This technique has proven enormously successful and is now the main line source of material for all PV-HgCdTe detector programs at SBRC. This material is of extremely high uniformity and produces very high performance detector arrays. It is therefore the surface and passivation of this material as it occurs in fabricated devices that we wish to characterize and eventually develop basic understanding of. The growth sequence for epitaxial HgCdTe layers consists of two parts: melt preparation and layer growth. First, liquidus and solidus points of the ternary phase diagram

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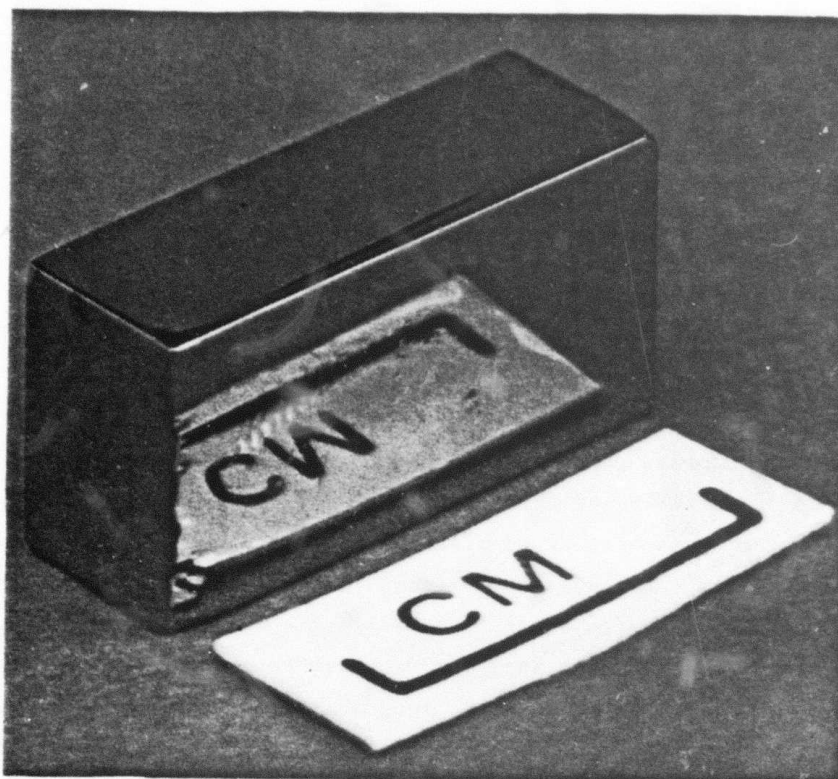


Figure 1. Block of Single-Crystal HgCdTe Oriented with Its Long Axis in the  $\langle 110 \rangle$  Direction

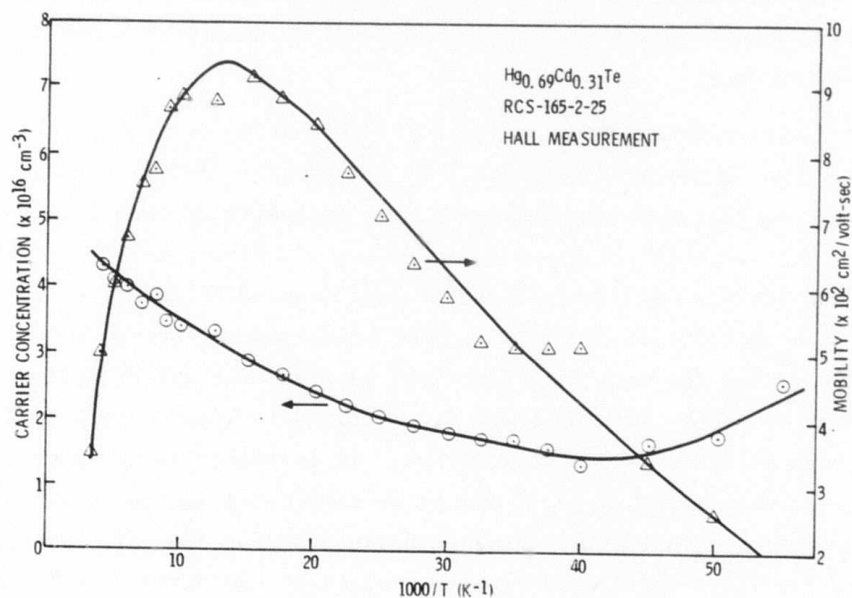


Figure 2. Carrier Concentration and Mobility of  $\text{Hg}_{0.69}\text{Cd}_{0.31}\text{Te}$  as Measured by the Hall Effect

Table 1. Cleaved Surface Characterization

Ingot	x	Type	Status	Source
I-CdTe	1	Intrinsic	Experiments Completed	Hughes Research Laboratory
II-CdTe	1	Lightly n-Type	Experiments Underway	Prof. Ebina
III-CdTe	1	p-Type	Experiments Completed	MIT
In: CdTe	1	$10^{17}$ n-Type	Experiments Underway	II-VI, Inc.
P: CdTe	1	$10^{17}$ p-Type	Experiments Underway	II-VI, Inc.
RCS-98 HgCdTe	0.2	$10^{16}$ p-Type	In Fabrication	SBRC
RCS-159 HgCdTe	0.22	$10^{16}$ p-Type	Experiments Underway	SBRC
RCS-144 HgCdTe	0.283	$10^{16}$ p-Type	In Fabrication	SBRC
RCS-129 HgCdTe	0.31	$10^{16}$ p-Type	Experiments Completed	SBRC
RCS-165 HgCdTe	0.31	$10^{16}$ p-Type	Experiments Completed	SBRC
RCS-185 HgCdTe	0.39	$10^{16}$ p-Type	Experiments Underway	SBRC

Table 2. Etched Surface Characterization

Substrate	Epi Layer	x	Type	Status	Source
1263-3 CdTe	VI-HCT-148-A2	0.35	$5 \times 10^{16}$ n-Type	Experiment Underway	SBRC
1263-3 CdTe	VI-HCT-148-B5	0.35	$5 \times 10^{16}$ n-Type	Experiment Underway	SBRC
RCS-92-40 HgCdTe	VII-HCT-41A	0.45	$1 \times 10^{16}$ n-Type	Experiment Underway	SBRC
RCS-92-34 HgCdTe	VII-HCT-41B	0.45	$1 \times 10^{16}$ n-Type	Experiment Underway	SBRC
ZH-143-5D	Bulk	0.2	$\sim 10^{15}$ p-Type	AES Completed	SBRC
RCS-78-78	Bulk	0.3	$\sim 10^{15}$ p-Type	AES Completed	SBRC

are determined, then the melt is prepared as to liquidus composition, growth temperature and furnace profile.

The actual growth of the epitaxial layer consists of immersing either a CdTe or HgCdTe substrate in the melt and growing for a specified length of time (several minutes to ~1 hours) to produce the desired epitaxial layer thickness. Once a melt has been established, it is used repeatedly for layer growth. Experience has shown that melt characteristics remain constant over long periods of time and can therefore be relied on to produce large numbers of layers with uniform properties. This feature will be key in correlating results on surfaces obtained with different techniques to the electrical properties of the interface as it occurs in electrical devices.

Figure 3 illustrates the repeatability of various layer growth compositions ( $\lambda_c$  value) in the 3- to 6- $\mu$ m range for different growth temperatures in the same melt. Growth compositions were repeatable over a period of more than 3 months. Figure 4 shows the repeatability of donor doping concentration obtained in grown epitaxial layers over a period of 30 days. The excellent uniformity of layer thickness and composition over a broad area is illustrated by Figures 5 and 6.

The "infinite" melts are always kept saturated and are maintained at the appropriate growth temperature between successive runs; substrates are introduced into the melt through an air lock. This technique allows several layers to be successively grown on the same substrate, but in different furnaces in a relatively short time. No time is required to bring various melts to equilibrium as with the conventional slide bar technique. Most importantly, large melts of ~4000 gms provide extremely uniform temperature control at the growth interface and result in layers with excellent compositional and thickness uniformity. The system design provides a stable high-purity environment for maintaining the established melt characteristics. The use of large melts results in a near constant saturation temperature from run to run and assures excellent layer repeatability since the amount of material removed from the melt during each growth run is relatively insignificant. These large melts additionally allow melt impurities to be accurately compensated.

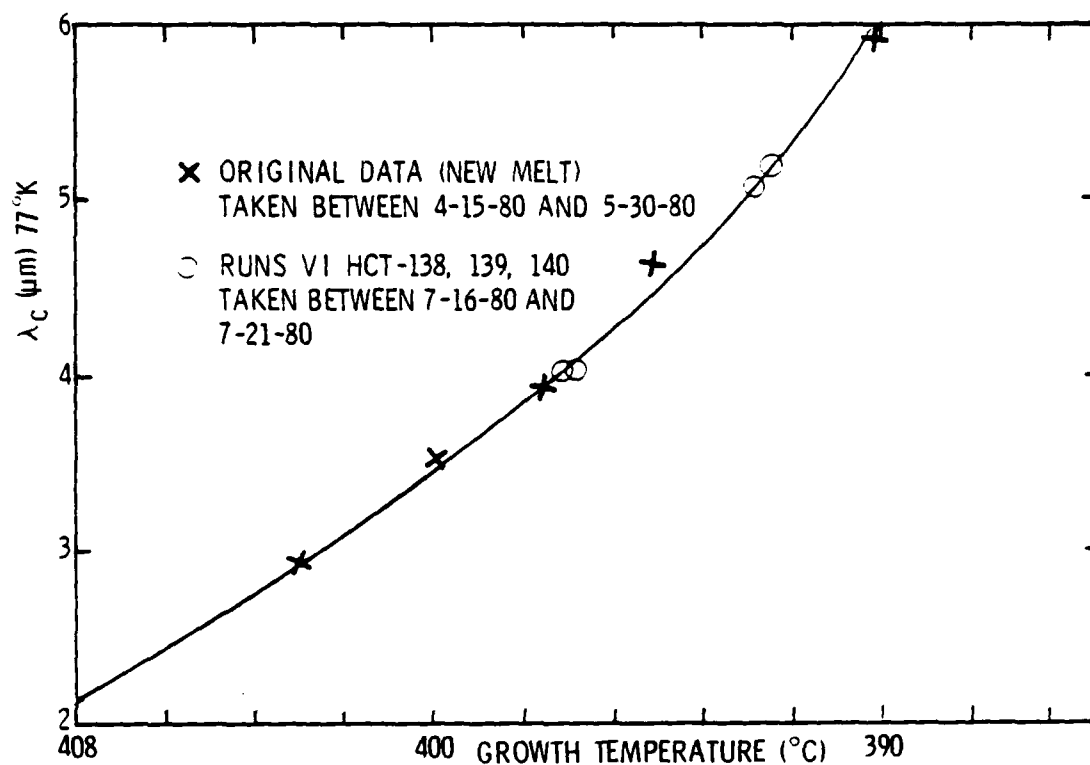


Figure 3. Compositional Uniformity of Infinite Hg Melt VLPE

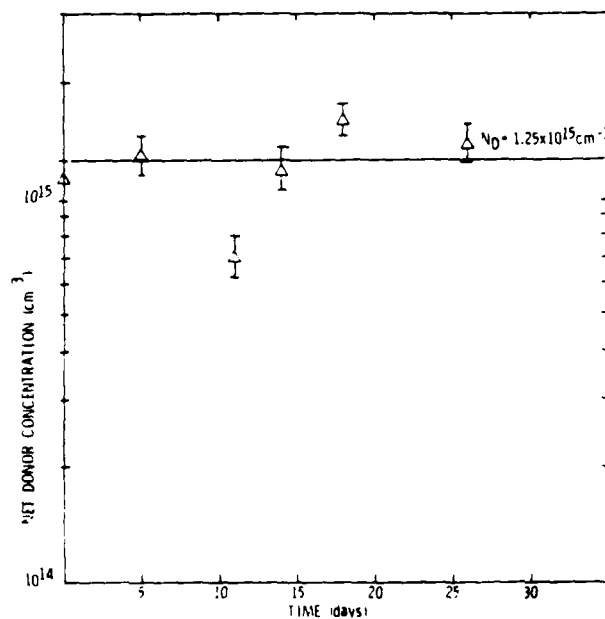
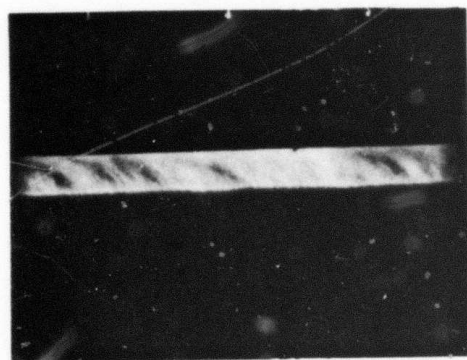


Figure 4. Stability of As-Grown Doping in Vertical Infinite Melt Hg LPE System



15  $\mu\text{m}$   
 $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$  LPE LAYER  
 CdTe SUBSTRATE  
 ● PLANAR / WELL-DEFINED INTERFACE  
 ● EXCELLENT SURFACE MORPHOLOGY

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Figure 5. Cross Sectional View of LWIR LPE Layers Grown from "Infinite" Hg Melt VLPE Systems

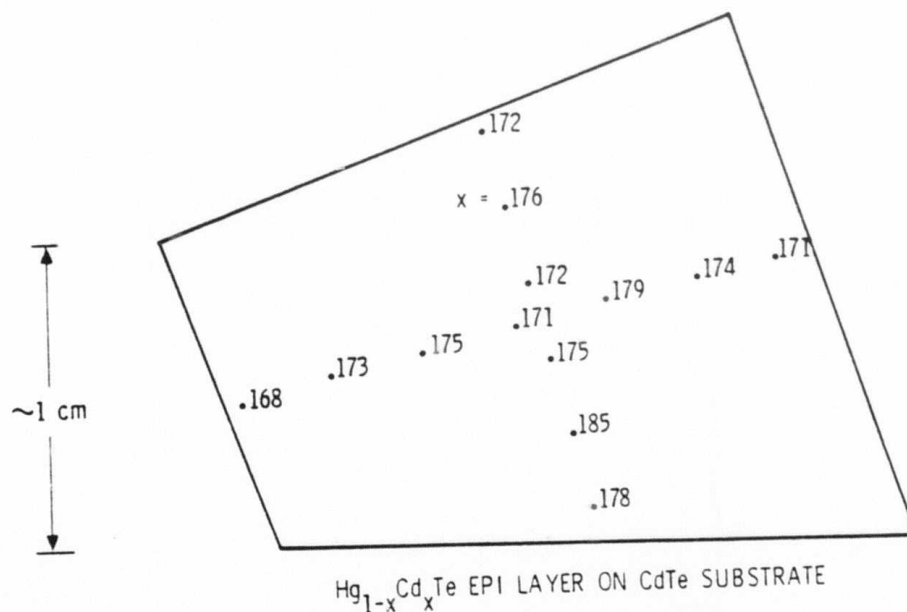


Figure 6. Uniformity of LWIR Epi Layer Composition Using Electron Microprobe

Anodic oxides layers have been grown on <111> oriented HgCdTe. These will be subjected to sputter Auger analysis to determine the oxide compositions. All the layers prepared are in the process of being tested, and results will be available soon. The oxide thicknesses as determined from ellipsometry are listed in Table 3.

Table 3. Anodic Oxide Characterization

Wafer Identification	x	Type	Orientation	Thickness (Å)	Status
RC-66-113	0.21	$3 \times 10^{15}$ n-Type	<111>	600	Sputter/Auger in Progress
RC-66-114	0.21	$3 \times 10^{15}$ n-Type	<111>	1035	Sputter/Auger in Progress
RCS-96-76	0.285	$2 \times 10^{16}$ p-Type	<111>	520	Sputter/Auger in Progress
RCS-96-77	0.285	$2 \times 10^{16}$ p-Type	<111>	995	Sputter/Auger in Progress
RC-66-115A	0.21	$3 \times 10^{15}$ n-Type	<111>	600	MIS in Testing
RC-66-115B	0.21	$3 \times 10^{15}$ n-Type	<111>	1060	MIS in Testing
RCS-96-75A	0.285	$2 \times 10^{16}$ p-Type	<111>	595	MIS in Testing
RCS-96-75B	0.285	$2 \times 10^{16}$ p-Type	<111>	1060	MIS in Testing



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### Section 3

#### EXPERIMENTS AND RESULTS

This section describes in detail the experiments and results of measurements on  $\text{Hg}_{0.69}\text{Cd}_{0.31}\text{Te}$  and  $\text{CdTe}$ . Tests on the other materials listed are currently underway and will complete the study of the atomically clean  $\text{HgCdTe}$  surface. The remainder of the program will deal with more realistic device surfaces such as the as-grown and etched surfaces.

#### PHOTOEMISSION ON $\text{CdTe}$

Valence electronic states were probed using UPS with light from a hydrogen discharge. The spectra obtained agree with past work done on this material and give additional information which will be useful in determining the contribution of  $\text{Hg}$  to the electronic structure of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ . It also gives baseline information for the investigation of  $\text{CdTe}$  as substrate material for  $\text{HgCdTe}$  epitaxial growth.

A clean  $\langle 110 \rangle$  surface was prepared by cleaving the crystals in a vacuum of  $5 \times 10^{-11}$  torr. Monochromatic light with energy between 6.0 and 10.4 eV was produced by hydrogen discharge and a McPherson 225 monochromator. The exit and entrance slits of the monochromator were adjusted to maintain a line width of 0.2 eV. The chamber was separated from the light source by a  $\text{LiF}$  window, and light normally incident on the sample. Energy distribution curves (EDC) were obtained using a four-grid electron spectrometer along with ac modulation and lock-in detection to differentiate the collected current. Energy resolution in the EDC is estimated to be 0.3 eV. Emission from a gold film previously evaporated on a stainless steel shutter, which could be swung in front of the grids, served to locate the position of the Fermi level to within 0.4 eV.

One aim in performing these measurements was to compare results with work done at the Stanford Electrical Engineering Laboratory in an earlier investigation.<sup>2</sup> While agreement between the two sets of experiments is good overall, it is felt that the present study benefits from the capability of a higher resolution electron analyzer as well as superior vacuum conditions and therefore

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<sup>2</sup>J.L. Shay, Photoemission Studies of the Electronic Structure of  $\text{CdTe}$ ,  $\text{CdSe}$ . Technical Report No. 5216-1 (1966).

surface cleanliness. In addition, Fermi level information, which will be made more accurate in future work, was not obtained in the earlier study.

The principal goal of the experiment was to obtain information on the valence band electronic states for CdTe, with the purpose of comparing these data to that to be obtained by repeating the experiment for  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  with values of  $x$  other than 1. Such a comparison will contribute to an understanding of the role of Hg in determining the electronic structure of the crystal and of the bonding and stability of Hg in the lattice. This comparison will be greatly facilitated by the availability of accurate band structure calculations for HgCdTe of different compositions. Since the late sixties, when the earlier study of CdTe was completed, improved band structure calculations for CdTe have been performed. Few recent calculations for  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  have been published, however. It is hoped that the availability of accurate photoemission measurements for this alloy system will stimulate theoretical efforts in this area. Further discussion of the band structure for CdTe will be deferred until accurate band structures for HgCdTe have been calculated.

#### PHOTOEMISSION ON HgCdTe

The stability of Hg in the alloy has been studied using ultraviolet and X-ray photoemission spectroscopy. A clean  $\langle 110 \rangle$  surface was prepared by cleaving single-crystal  $\text{Hg}_{0.69}\text{Cd}_{0.31}\text{Te}$  in vacuum. The composition of the surface region was monitored by measuring the emission from Hg and Cd "d" levels near the bottom of the valence band. Figure 7 shows EDCs taken on cleaved surfaces of CdTe and  $\text{Hg}_{0.69}\text{Cd}_{0.31}\text{Te}$ . Photons of energy 21.2 eV were incident on the surface, and the number of emitted electrons as a function of their kinetic energy were recorded. The resulting curves for the two materials have been positioned so that their emission edges coincide at 14.7 eV, which corresponds to the valence band upper edge, and normalized to the same valence band peak height. Emission from states in the valence band is seen between 8.5 and 14.7 eV. The core levels observable with this incident energy are Cd (4d) and Hg(5d) which are seen as peaks below 8.5 eV. From observation of the amplitude of these peaks over several days, no loss of Hg from the surface region of the freshly cleaved surface in a vacuum was detected.

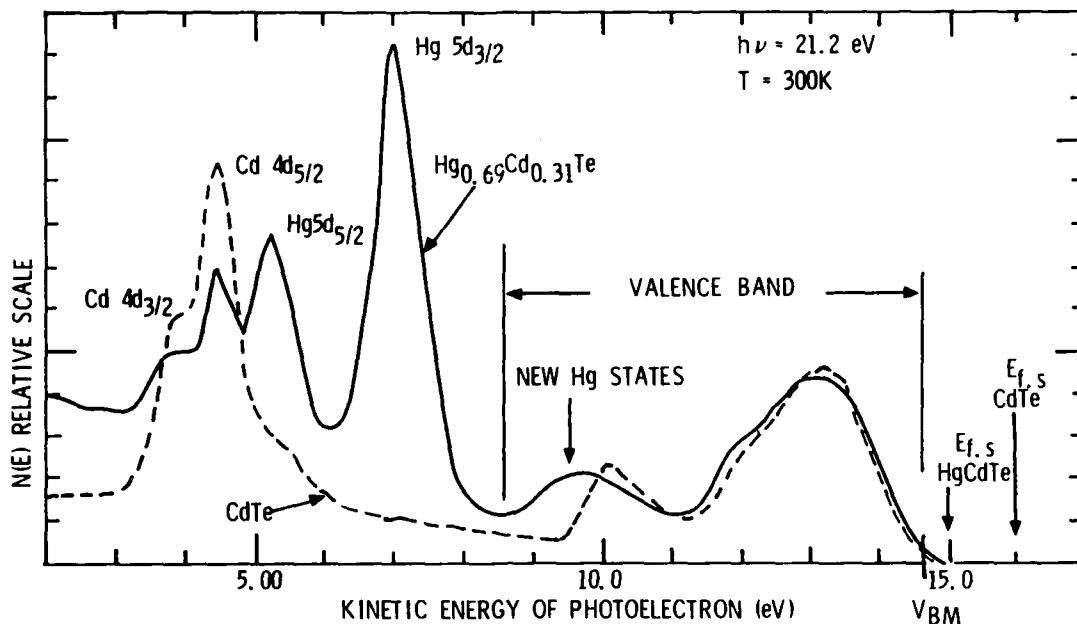


Figure 7. Energy Distribution Curves (EDC) Resulting from Photoemission Spectroscopy on Cleaved  $\text{Hg}_{0.69}\text{Cd}_{0.31}\text{Te}$  and CdTe

The adsorption of oxygen on a clean  $\text{Hg}_{0.69}\text{Cd}_{0.31}\text{Te}$  surface has also been investigated. Exposure to up to 1 atm of unexcited oxygen for 16 hours produced no measurable adsorbed oxygen. Exposure to oxygen excited by an ion gauge, however, did result in oxygen uptake and changes in the composition of the surface region.

A single-crystal sample of  $\text{Hg}_{0.69}\text{Cd}_{0.31}\text{Te}$  was transferred into the vacuum chamber from air through a vacuum interlock. By obtaining ultra-high vacuum ( $5 \times 10^{-10}$  torr) in the experimental chamber before introduction of the sample, raising the crystal to elevated temperatures was avoided. A clean  $\langle 110 \rangle$  surface was prepared by cleaving in vacuum. UPS was performed using light of 21.1-eV photon energy and taking EDCs using a double-pass cylindrical mirror electron energy analyzer with 0.1-eV energy resolution. This choice of photon energy permits observation of the emission from states with binding energies up to 16 eV below the valence band maximum. This region includes the valence band and the Cd(4d) and Hg(5d) core levels. The position of the Fermi level was determined from the edge of emission of a gold film evaporated on a stainless-steel substrate in electrical contact with the sample. An example of the EDC obtained for Au is shown in Figure 8 compared to  $\text{HgCdTe}$ . Spectra of a cleaved  $\langle 110 \rangle$  surface were also obtained for p-type CdTe.

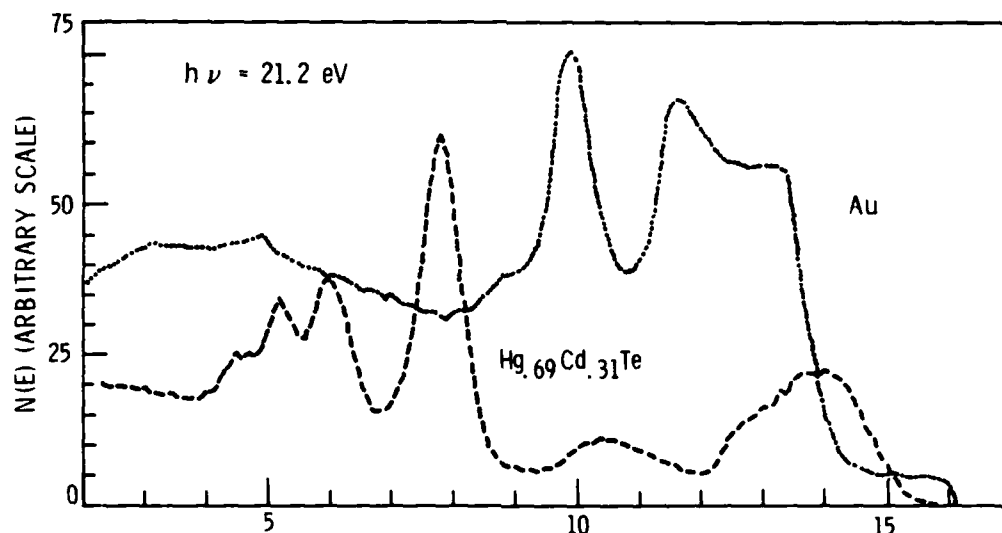


Figure 8. EDC of Au Shown Compared to  $\text{Hg}_{0.69}\text{Cd}_{0.31}\text{Te}$

After 5 hours of observation of the clean surface, during which no evidence of Hg loss was found, the sample was exposed to high-purity molecular oxygen. Care was taken in this series of exposures that no source of excitation for the oxygen molecules was present in the chamber. EDCs were recorded with 21.2-eV photons for the HgCdTe and the gold film following exposures of up to  $4 \times 10^{13}\text{L}$  (1 Langmuir =  $10^{-6}$  torr-sec). Exposures were not performed at constant pressure. The chamber pressure varied through a range of exposures from 10L (at  $10^{-7}$  torr) to  $4 \times 10^{13}\text{L}$  (at 1 atm) which were monitored in turn by a cold cathode ionization gauge, DV-4 thermocouple gauge, and molecular pressure gauge.

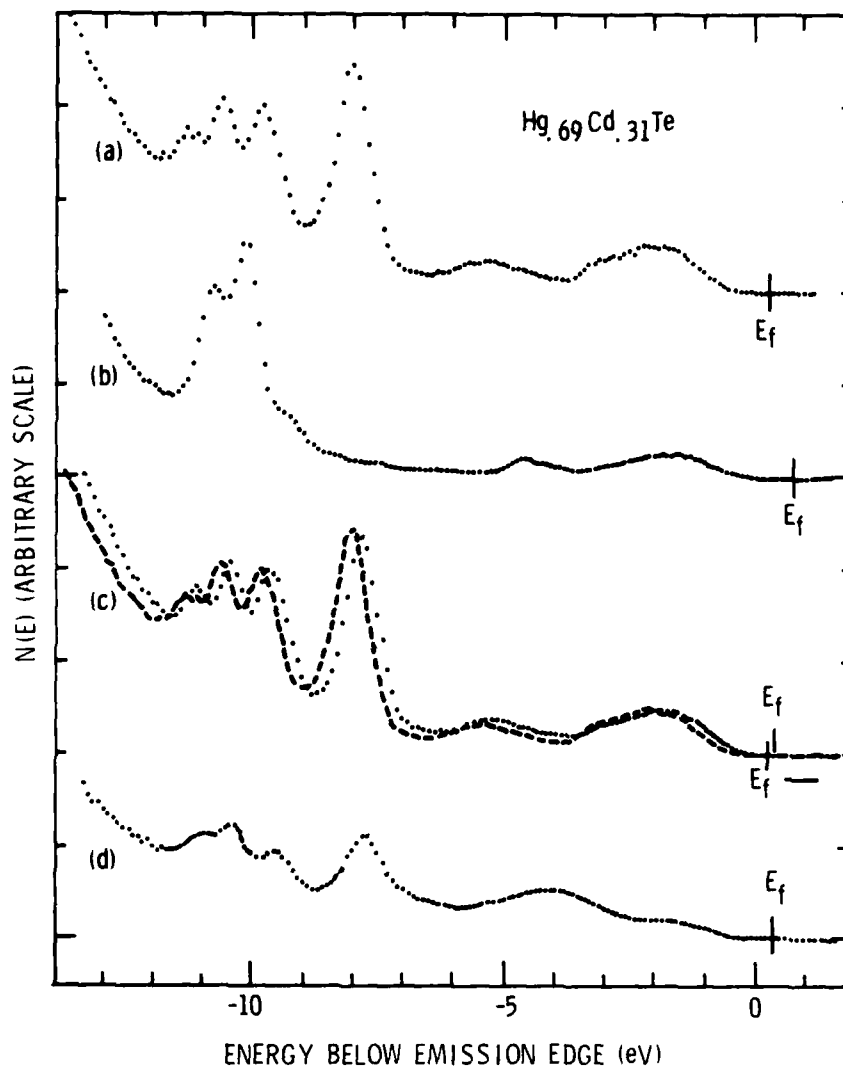
Experiments were resumed two days after completion of the UPS measurements following the largest exposure to unexcited oxygen. The UPS measurements were repeated for this surface, and the surface was examined for oxygen and contaminants by XPS using Mg K-alpha radiation (1253 eV). Emission from the Te(3d), Cd(3d), and Hg(4f) core lines was also recorded. Because of the absence of evidence of oxygen or other contamination, a second series of oxygen exposures was initiated on the same surface rather than on a fresh cleave. In this instance, oxygen was admitted to the chamber in the presence of the discharge of a hot filament ionization gauge. For exposure to  $3 \times 10^6\text{L}$ , the discharge current from the filament was 9 ma. For the higher pressure exposure to  $4.1 \times 10^8\text{L}$ , 0.4-ma discharge current was used. After both exposures, UPS measurements of the valence bands, upper core levels, and the gold film were performed; and XPS spectra of the Te(3d), Cd(3d), and Hg(4f) lines were recorded.

## RESULTS

Comparison of photoemission spectra of HgCdTe and CdTe can provide information on the contribution of Hg to the electronic structure of the alloy. Because the Hg(5d) and Cd(4d) core levels lie within 12 eV of the valence band edge, UPS with 21.2-eV photons can be used to monitor relative change in concentration such as would occur with preferential Hg out-diffusion. The EDC of clean cleaved p-type HgCdTe is shown in Curve a of Figure 9 and the spectrum for p-CdTe is represented for comparison in Figure 9b. The spectra have been aligned at the edge of emission, which is taken to be the zero of energy. The Fermi level is indicated, and in both cases the Fermi level at the surface appears pinned. The data suggest that the surface converts to n-type on cleaving, but the valence band maximum must be located more exactly and experiments must be performed as a function of temperature before this can be proven as sure. Emission at 10.6 and 11.3 eV in the alloy spectrum arises from Cd(4d) levels. The Hg(5d) core lines appear at 8.0 and 9.9 eV. While structure in the upper portion of the valence bands appears quite similar, additional states can be seen for HgCdTe near the lower edge of the bands (see Figure 7). Presumably, differences in electronic structure are due to the bonding of Hg in the lattice. Emission from the Hg and Cd d bands remained constant during the 5 hours used to study the clean surface. No evidence of loss of Hg was observed.

The cleaved <110> surface proved extremely inert to adsorption of unexcited molecular oxygen. The UPS spectrum taken following exposure to  $4 \times 10^{13}$  L (16 hours at 1 atm of oxygen) is given by the solid curve in Figure 9c. The spectrum of the clean surface, shown dashed, has been shifted horizontally to facilitate comparison. The curves presented in Figure 9c have been normalized to the height of the Cd(4d) peak. The ratio of the areas of the Cd(4d) and Hg(5d) peaks agree in the two cases to within 1%, and no changes in the valence band structure are observed. The spectrum for the highest unexcited oxygen exposure was recorded following a lengthy series of exposures and characterizes the surface region 120 hours after cleaving.

Exposure to  $4.2 \times 10^8$  L produced an oxygen-induced structure in the valence band at 4.1 eV, as shown in Figure 9d. For exposure to  $3 \times 10^6$  L excited oxygen and, as shown in the figure, for exposure to  $4.2 \times 10^8$  L, the Hg(5d) emission decreased relative to the Cd(4d) line. In addition, it is assumed that the



- a) Clean  $\langle 110 \rangle$  Surface of  $\text{Hg}_{0.69}\text{Cd}_{0.31}\text{Te}$  Cleaved in Vacuum
- b) Clean  $\langle 110 \rangle$  p-CdTe Cleaved in Vacuum
- c) Comparison of  $\text{Hg}_{0.69}\text{Cd}_{0.31}\text{Te}$  following exposure to  $4 \times 10^{13} \text{L}$  Unexcited Oxygen (Solid) and Clean Spectrum of Curve (a) (Dashed)
- d)  $\text{Hg}_{0.69}\text{Cd}_{0.31}\text{Te}$  Following Exposure to  $4.2 \times 10^8 \text{L}$  Excited Oxygen

Figure 9. UPS Spectra of HgCdTe at 21.2 eV

broad new peak which appears at 4.1 eV is due directly to chemically-bound oxygen. The absence of these features in the case of even large exposures to molecular oxygen confirms the inertness of the surface to oxygen uptake and the ability to detect Hg loss, should it occur.

XPS results for the surface exposed to  $4 \times 10^{13}$  L unexcited oxygen, and the two exposures to excited oxygen, confirm the composition changes observed in the UPS spectra. Relative to the signal from the Te(4d) peak, the Cd(3d) emission increases with each exposure to excited oxygen, while the Hg(4f) levels show a diminished intensity after exposure to  $3 \times 10^6$  L. Exposure to  $4.2 \times 10^8$  L increased emission from the Hg(4f) level over the  $3 \times 10^6$  L case, but the intensity was still less than that for the  $10^{13}$  L surface. A chemical shift of 3.5 eV to higher binding energy was observed for the Te(4d) levels. The area under the shifted peaks was approximately 9% of that for the Te in the alloy. No other chemical shifts were observed. Thus, it is concluded that only Te oxide was formed.

Future studies will systematically investigate composition changes and oxygen uptake for clean surfaces exposed to excited oxygen. The present experiment indicates that the unperturbed cleaved surface is stable under vacuum and that out-diffusion of Hg does not occur.  $\text{Hg}_{0.69}\text{Cd}_{0.31}\text{Te}$  is surprisingly insensitive to oxygen in the molecular ground state; however, exposure to excited oxygen produces Te oxide.

#### AES MEASUREMENTS OF DAMAGED SURFACE

Ion bombardment serves as a controllable measure of perturbing the surface region in order to study the effect of damage to the surface on the properties of the surface region. The effect of ion bombardment on the surface composition must also be studied to accurately apply depth profiling techniques and to determine the suitability of sputtering for preparing clean surfaces for surface studies of epitaxial layers. Auger electron spectroscopy has been used to analyze changes in the composition of the surface of epilayers subjected to ion bombardment.

#### Experiment

Epitaxial samples of  $\langle 111 \rangle \text{Hg}_{1-x}\text{Cd}_x\text{Te}$  with  $x = 0.2$  and  $0.3$  were placed in the experimental chamber without being subjected to temperatures above room temperature. The base pressure in the chamber was  $1 \times 10^{-9}$  torr. Neon (Ne) gas



was admitted to the chamber and the ion pump turned off until the pressure rose to  $4 \times 10^{-5}$  torr. A cryopanel cooled by liquid nitrogen was used to maintain low partial pressures of residual impurity gases. During sputtering, the sample was bombarded by 1-keV Ne ions at an ion current density of  $7.4 \times 10^{-6}$  A/cm<sup>2</sup>. Auger analysis was performed using a single-pass cylindrical mirror analyzer with integral electron gun. Measurements were made with a  $2 \times 10^{-6}$  A electron beam at 5 kv. There was no indication of electron beam artifacts during the experiment. The peak-to-peak heights in the derivative spectrum of Auger transitions for Hg (76 and 2078 eV), Te (483 eV), C (276 eV), S (152 eV), and O (510 eV) were electronically determined, and a plot made of the peak-to-peak heights as a function of time for these transitions. In addition, detailed spectra were obtained of the original surface, during sputtering, and after sputtering.

### Results

Figure 10 presents the peak-to-peak heights (arbitrary scale) of the transitions monitored as a function of ion fluence in ions/cm<sup>2</sup> for Hg<sub>0.7</sub>Cd<sub>0.3</sub>Te; the results for the x = 0.2 sample are given in Figure 11. The surface had been etched in a bromine-methanol solution and exposed to ambient air for several weeks. The surface prior to sputtering showed significant amounts of carbon as well as some oxygen and sulfur. These signals dropped below the detectable level within 1 minute of the onset of sputtering, indicating the film of contaminants to be very thin (<20Å). The composition measured during sputtering stabilized after a dose of approximately  $10^{16}$  ions/cm<sup>2</sup>.

Calculation of the relative composition of the samples did not yield the stoichiometric composition. It is believed that this error is due to inaccuracy in the sensitivity factors used in the calculation. For a given set of sensitivities, however, relative changes of composition can be determined. The Te concentration was found in this way to be constant in the presence or absence of ion bombardment. The calculated value for Cd increased during ion bombardment. The concentration of Hg using the 76-eV line and the 2078-eV line showed opposite tendencies; the 76-eV line, which is more sensitive, gave an increase in Hg during sputtering, while the higher energy line, which probes a deeper region of the surface, indicated a decreased Hg concentration. These results suggest that ion bombardment significantly perturbs the composition of the surface region. To ensure that these changes were not due to an increase

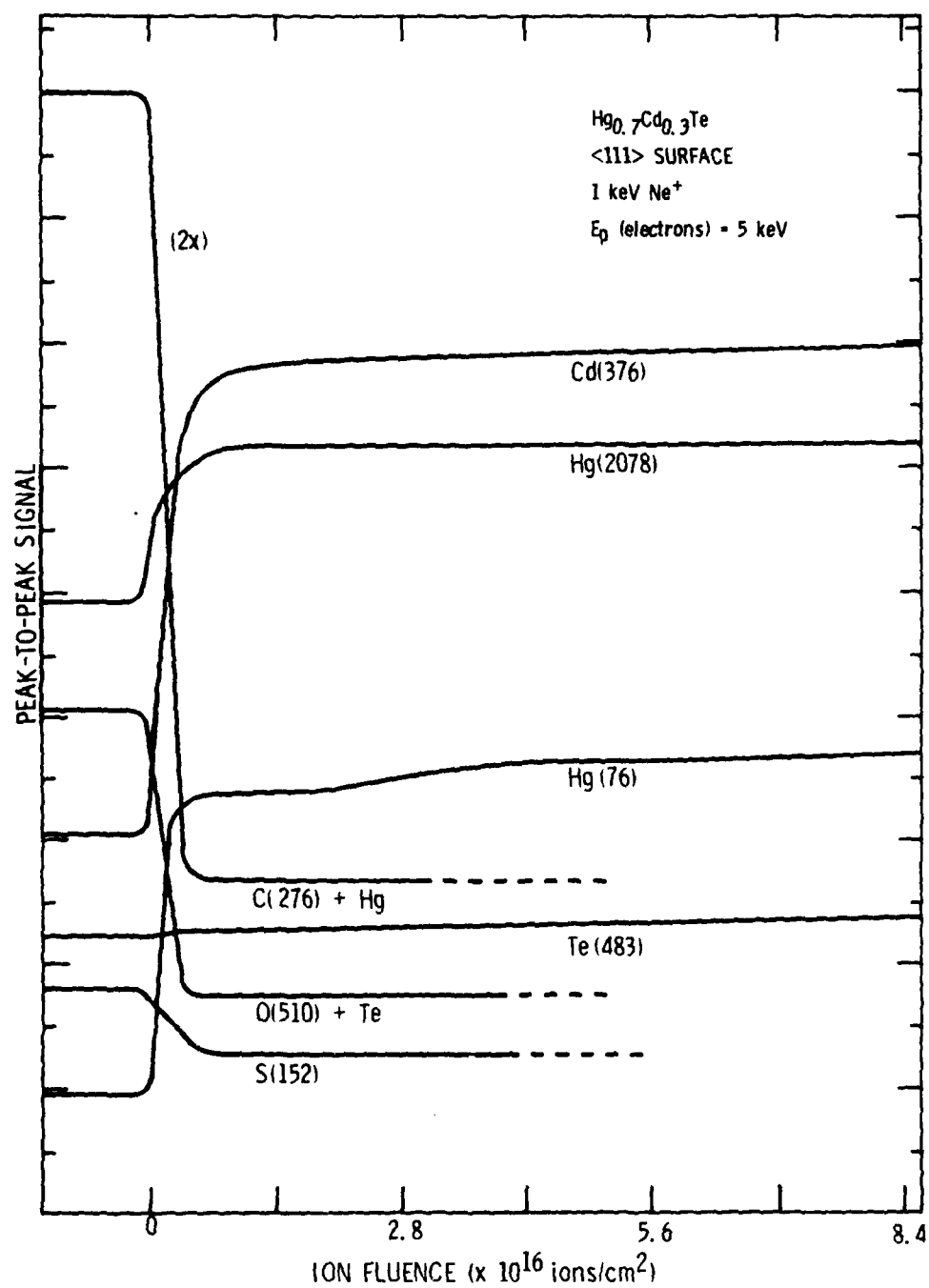


Figure 10. Auger Peak-to-Peak Heights (Arbitrary Scale) versus Ion Fluence (ions/cm<sup>2</sup>) for Epitaxial  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$

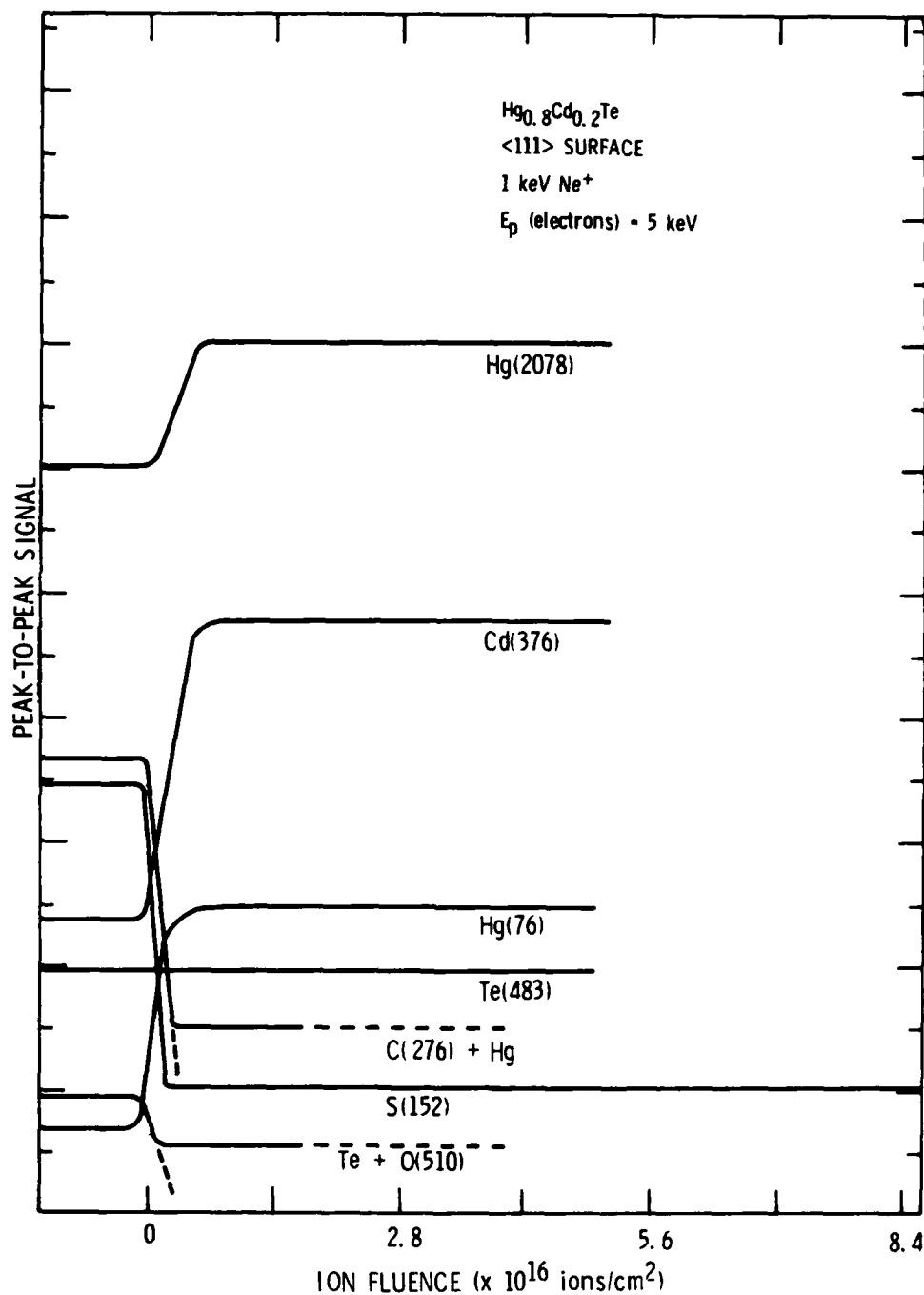


Figure 11. Auger Peak-to-Peak Heights (Arbitrary Scale) versus Ion Fluence (ions/cm<sup>2</sup>) for Epitaxial  $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$

in measured peak-to-peak height due to line shape changes, the derivative spectra were numerically integrated. Comparison of the areas under the Auger peaks in the integral of spectra recorded during and after sputtering confirmed the above conclusions.

Additional work must be done to accurately calibrate Auger measurements on HgCdTe. Future studies will continue to examine the compositional changes which apparently take place during sputtering.

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#### Section 4 CONCLUSIONS

The results described in the previous section were obtained on the cleaved  $\langle 110 \rangle$  surface of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  with  $x = 0.31$ , and the epitaxial  $\langle 111 \rangle$  surface with  $x = 0.2$  and  $0.3$ . It has been seen that the cleaved surface is stable against Hg loss in a high vacuum, though there does appear to be an excess of Hg in the region near the surface which possibly causes the surface to be n-type. Changes in composition and chemistry resulted from damage to the structure of the surface region.

No uptake of oxygen was seen on the vacuum cleaved surface after exposure to dry molecular oxygen. Oxygen excited by the filament of an ion gauge resulted in the formation of a layer of Te oxide on the surface. No evidence of free Hg or Cd metal was seen nor were these oxides evident.

Future studies will detail the effects of mechanical damage on the surface composition and chemistry. These changes in composition will be correlated to the surface electrical properties by carefully monitoring changes in the Fermi level position at the surface.

Initial sputter Auger analysis of two lightly etched epitaxial surfaces indicates that changes in composition are induced by ion bombardment. These changes will be quantified in future work. Auger analysis before ion bombardment did not yield the stoichiometric ratio, indicating a need to calibrate the sensitivity factor used in the data analysis.

The studies of the electronic structure of the "perfect" surface will be expanded to cover all the samples listed in Table 1. Changes in electronic states which result from damage and oxidation will be measured. Photoemission spectroscopy and other studies will be extended to "nonperfect" (as-grown epitaxial and processed) surfaces.

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Section 5  
PROPOSED EFFORT FOR THE NEXT REPORTING PERIOD

During the next reporting period (ending 1 September 1981) the surface study program will concentrate on the following areas:

- Continue photoemission studies of the band structure of HgCdTe and CdTe, utilizing lamp and synchrotron sources.
- Extend these measurements to include HgTe.
- Photoemission studies of the oxidation of clean HgCdTe will expand to cover the entire range of x values from 0.2 to 0.39.
- Continue to investigate the effects of sputtering on HgCdTe stoichiometry.
- Investigate the composition of anodic oxide on HgCdTe by sputter/Auger.
- Evaluate electrical characteristics of MIS devices, incorporating the anodic oxide, with C-V analysis.
- Develop a method of transporting LPE-grown HgCdTe to Stanford in vacuum. This is to ensure a supply of unoxidized clean epi surfaces for investigation.



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